



# Metal surface modification with fatty acids using ionising radiation

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## INTRODUCTION

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material (usually a metal) or its properties because of a reaction with its environment.

Metals are used in a wide range of applications. Accordingly they are often exposed to aggressive environments and thus the corrosion is enhanced. Expenses occurring because of corrosion cost more than 3% of the world's GDP. This is why studying the modification of the metal surface and enhancing the protective properties of a metal is needed.

Copper and its alloys are employed in a myriad of end-uses: from common household electrical wiring to boat propellers and from photovoltaic cells to saxophones.

Fatty acids are non-toxic compounds which have an affinity for self-assembling on metals and therefore lately they have been investigated as possible protective layers on metals. Elaidic acid is a monounsaturated (one *trans* double bond) fatty acid found in hydrogenated vegetable oils.

The influence of ionizing radiation on the formation of such a layer is interesting since it does not markedly influence the properties of the metal but it does influence the protective layer that is formed on its surface.

## EXPERIMENTAL

**Electrode:** Cu (99.9%)

**Counter electrode:** Pt electrode

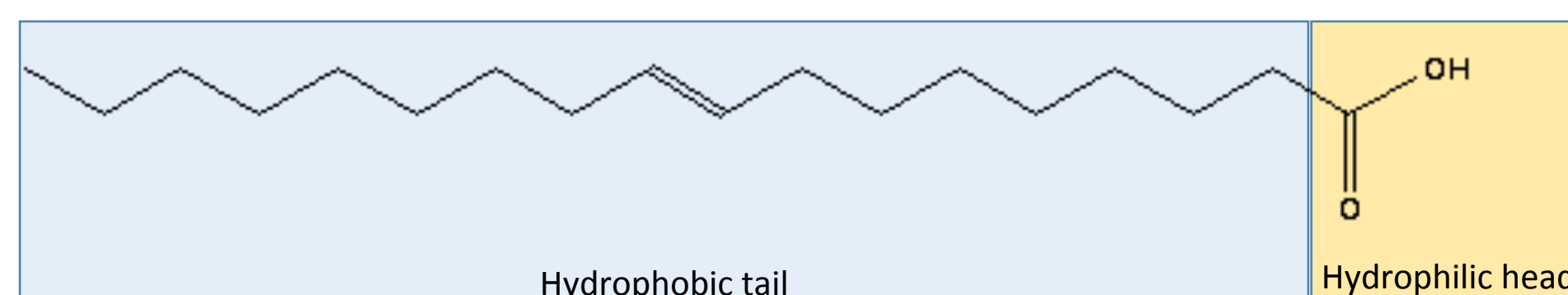
**Reference electrode:** SCE

**Electrolyte:** 3 % NaCl

**Inhibitor:** Elaidic acid (EA),  $\text{CH}_3(\text{CH}_2)_7\text{CHCH}(\text{CH}_2)_7\text{CO}_2\text{H}$  dissolved in ethanol at  $c = 0.001 \text{ mol/L}$

**Preparation of treated samples:**

- Copper samples heated in furnace for 4h at 75 °C
- Immersed in EA/EtOH for 18h at 40 °C
- Drying in air at room temperature
- Gamma irradiated in air with 0.1, 1, 3, 5, 7, 10 kGy at 30.98 kGy/h



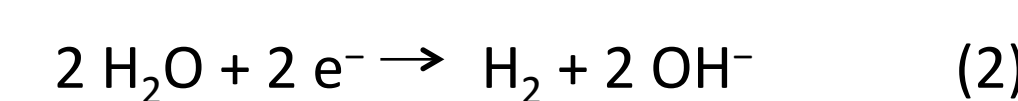
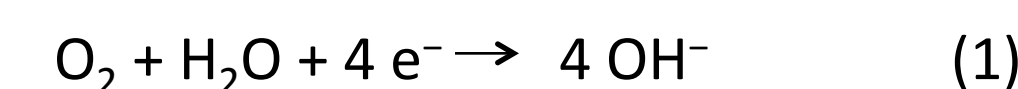
**Methods:**

- Tafel extrapolation method ( $0.16 \text{ mVs}^{-1}$ ;  $\pm 150 \text{ mV oc}$ ) - PAR 263A Potentiostat/Galvanostat
- FTIR spectroscopy - Tensor II, Bruker equipped with ATR

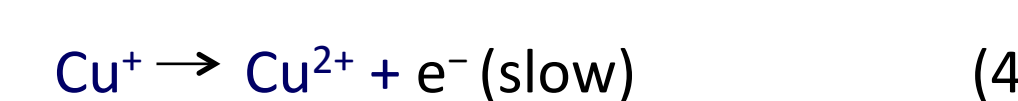
## CORROSION REACTIONS

**Copper corrosion reactions in aerated 3% NaCl solution**

*Cathodic reactions* – oxygen or water reduction



*Anodic reactions*



Cuprous cation,  $\text{Cu}^+$ , reacts in a fast reaction with  $\text{Cl}^-$  from the solution to form a partially protective layer of  $\text{CuCl}$  on the copper electrode surface:



The formed  $\text{CuCl}$  transforms to the soluble cuprous chloride complex:



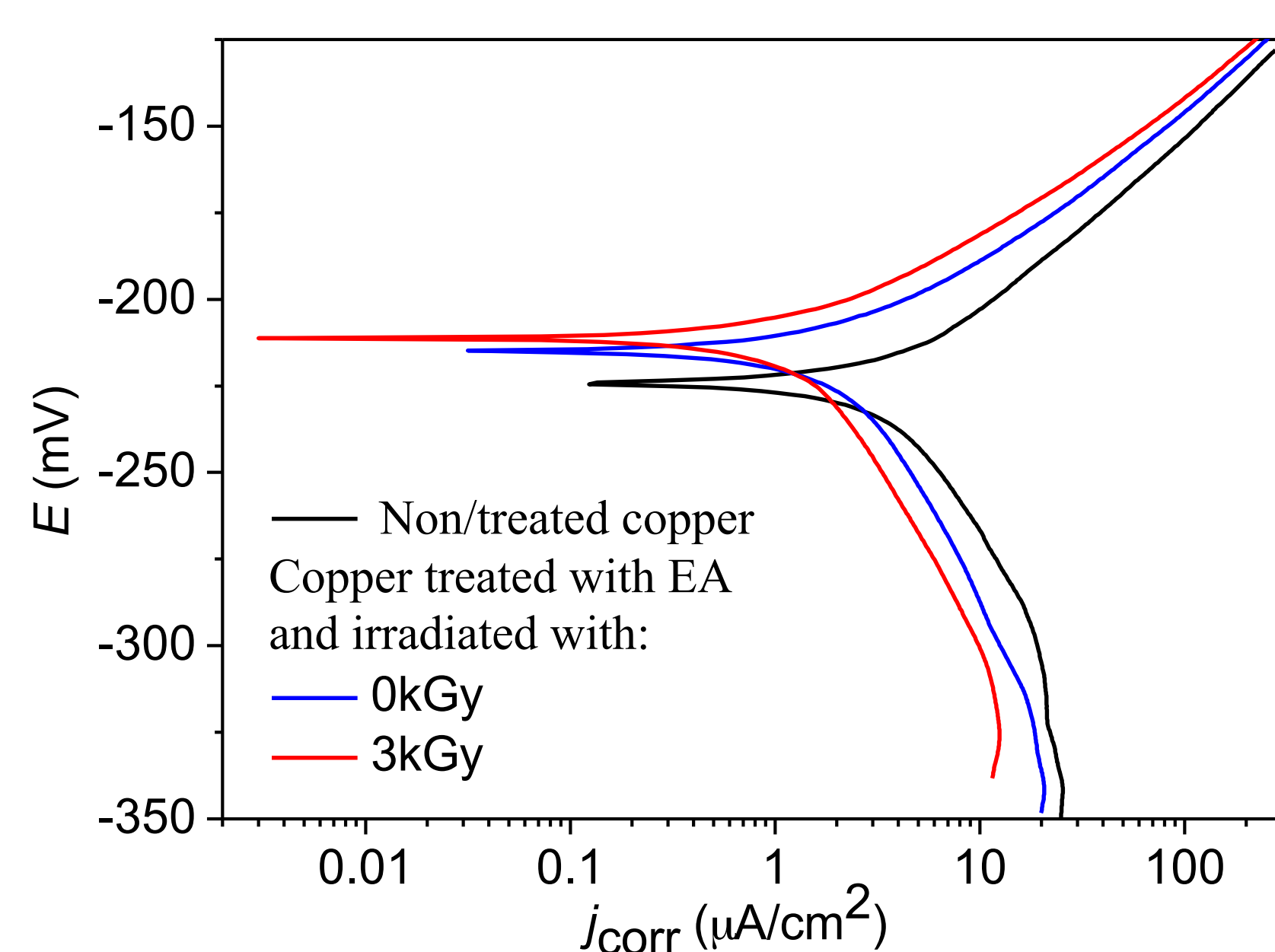
Once  $\text{CuCl}_2^-$  is formed at the surface of copper electrode, it will diffuse into the bulk solution or will dissolve by oxidation causing the copper dissolution:



## RESULTS

### POTENTIODYNAMIC MEASUREMENTS – Tafel Extrapolation Method – Determination of the optimal irradiation dose

Copper samples with adsorbed EA were irradiated by different doses and compared to the non-irradiated sample with an EA film on the surface and with the non-treated copper sample.



	D, kGy	$E_{corr}$ , mV	$b_a$ , mV dec <sup>-1</sup>	$-b_c$ , mV dec <sup>-1</sup>	$j_{corr}$ , μA/cm <sup>2</sup>
-	-	-236	76	240	5.470
Elaidic acid (EA)	0	-215	46	137	2.811
	0.1	-222	45	104	2.682
	0.5	-222	41	101	1.703
	1	-202	30	105	1.684
	3	-211	38	104	1.514
	5	-215	41	124	1.709
	7	-206	37	119	2.593
	10	-208	44	132	3.054

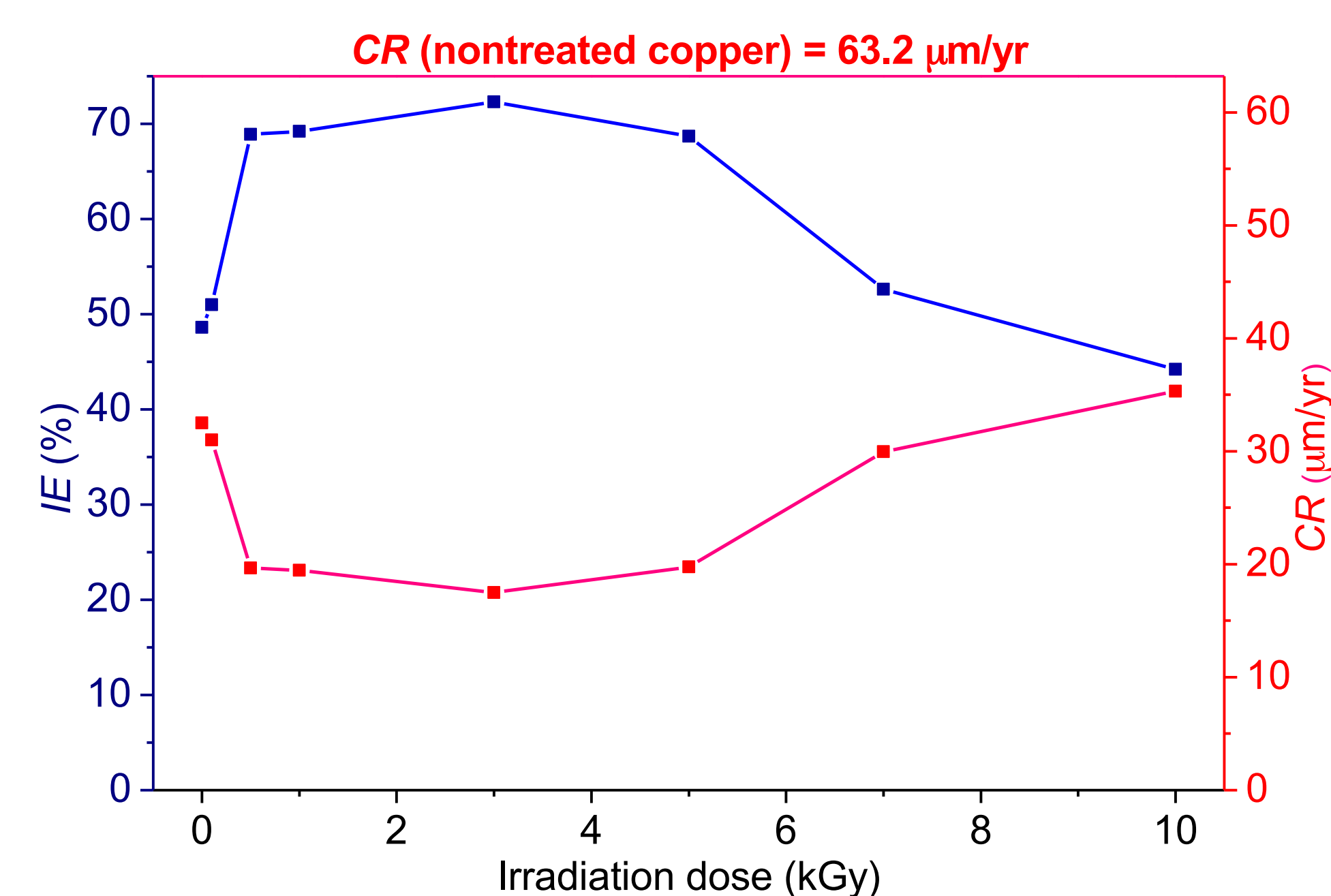
- It is clear that the highest cathodic and anodic currents are recorded for copper in NaCl solution in absence of EA. The lowest currents are observed on the samples that have been irradiated after EA adsorption.
- The lowest  $j_{corr}$  is observed on the sample irradiated with 3 kGy.
- A potential shift in the more noble direction, i.e. toward more positive potentials, is also clear when EA is present on the surface.
- Presence of EA on the surface decreases both Tafel slopes,  $b_a$  and  $b_c$ , indicating that both processes progress slower when EA is present on the surface.
- In order for the cathodic reduction of  $\text{O}_2$  (1) and  $\text{H}_2\text{O}$  (2) to take place they need to be present, i.e. adsorbed, on the surface of copper. The rate of this process is observed through the cathodic Tafel slope,  $b_c$ , which decreased in presence of EA. It is further more clear that after irradiation the slope decreases even more which indicates presence of a film on the surface of copper that has even better protective and hydrophobic properties.

$$IE = \frac{j_{corr}^0 - j_{corr}}{j_{corr}^0} \cdot 100\%$$

$IE$  [%] – inhibitor efficiency  
 $j_{corr}^0$  [μA/cm<sup>2</sup>] – corrosion current density of non-treated copper  
 $j_{corr}$  [μA/cm<sup>2</sup>] – corrosion current density of copper treated with EA

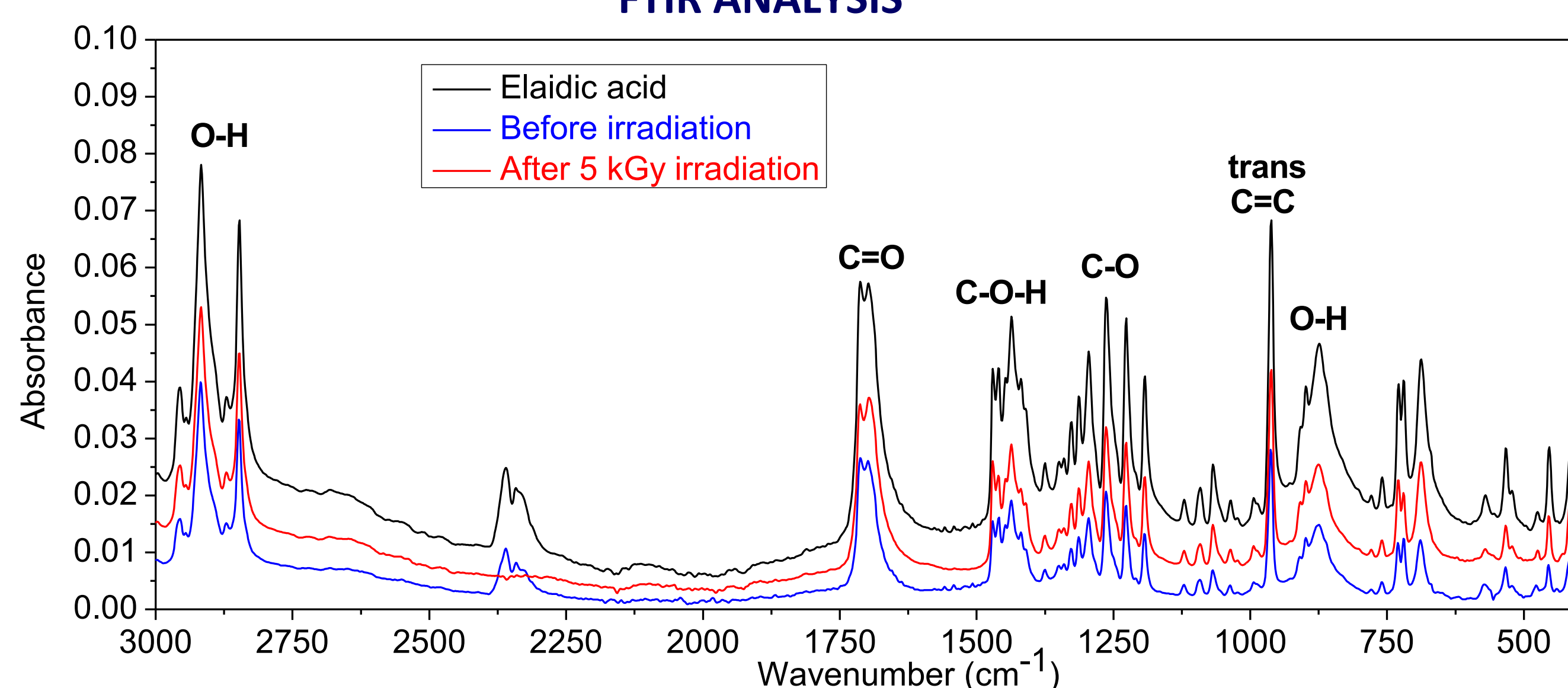
$$CR = \frac{M}{nF\rho} \cdot j_{corr}$$

$CR$  [μm/yr] – corrosion rate  
 $M = 63.55 \text{ g/mol}$  – molar mass of copper  
 $n$  – number of electrons transferred  
 $F = 96485 \text{ C/mol}$  – Faraday's constant  
 $\rho = 8.96 \text{ g/cm}^3$  – copper density

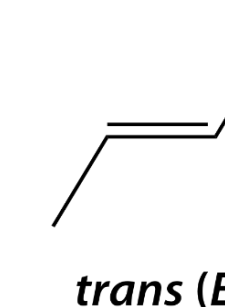
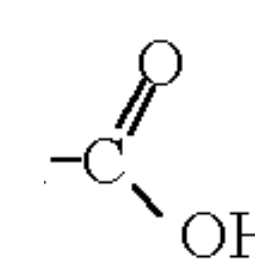


- Irradiation from 1 to 5 kGy all showed good protective properties with rather small variations in efficiencies, with a maximum at the dose 3 kGy and an inhibition efficiency of 72%.
- The corrosion rate clearly decreases from 63.2 μm/yr when copper is non-treated to values that are below 35 μm/yr. At the doses that showed best properties (1-5 kGy) the corrosion rate is three times smaller.

### FTIR ANALYSIS



- FTIR spectra obtained on samples with a EA surface film non-irradiated and irradiated both showed the main carboxylic acid bands representing stretching of OH (from 2966 to 2831  $\text{cm}^{-1}$ ), C=O (1712  $\text{cm}^{-1}$ ) and C-O (1262  $\text{cm}^{-1}$ ), as well as C-O-H (1436  $\text{cm}^{-1}$ ) and O-H (875  $\text{cm}^{-1}$ ) bend.
- The C=C double bond is characterized by a strong band representing the trans isomer (961  $\text{cm}^{-1}$ ).
- There is no significant difference between the bands of the irradiated and non-irradiated samples indicating that irradiation does not change the adsorbed molecules but rather influences the adsorption itself.



## CONCLUSIONS

- Elaidic acid (EA) a monosaturated fatty acid has been studied as a potential corrosion inhibitor for copper. It has been applied on the surface of copper by a slightly modified procedure that has been studied previously [1].
- The influence of gamma irradiation on the surface layer formed by EA has been investigated as a possibility to enhance the properties of the layer using gamma irradiation.
- Results have shown that irradiation at doses from 1 to 5 kGy enhance the protective properties of the EA surface layer. The best properties were obtained when irradiated with 3 kGy, where the corrosion inhibitor efficiency is 72%.
- FTIR analysis of the treated surface layers have shown that irradiation does not induce any significant change in the molecules adsorbed on the surface. It can be concluded that irradiation influences the strength of adsorption.